Flory. Detergency studies on the individual fractions indicate optimum soil removal at approximately seven ethenoxy units and optimum whiteness retention at about four ethenoxy units.

REFERENCES

1. Ballun, A. T., Bartels, G. E., and Karabinos, J. V., Trans. Ill. Acad. Sci., *47*, 81 (1955).
2. Flory, P. J., J. Am. Chem. Soc., 62, 1561 (1940).
3. Curme, G. O. Jr., and Johnston, F., "Glycols," Reinhold Publishing Corporation, New York, N. Y., p. 182 (1952).
4. Karabinos, J. V., Bartels, G. E., and Kapella, G. E., J. Am. Oil Chemists' Soc., *31*, 419 (1954).
5. Vaughn, T. H., and Suter, H. R., J. Am. Oil Chemists' Soc., *27*, 249 (1950).
6. Bramston-Cook, H. E., "Versatility of Nonionic Surfactants," presented to the American Soap and Glycerine Producers Asso. Inc., New York City, Jan. 28, 1955, p. 4.

[Received January 6, 1956]

Determination of Soaps by Ion Exchange Resins

J. W. JENKINS, Colgate-Palmolive Company, Jersey City, New Jersey

SALTS OF ORGANIC ACIDS are commonly analyzed by by combustion to the sulfate or carbonate (1, 2). The sulfate is determined gravimetrically while the carbonate is determined by the usual volumetric procedure. Non-aqueous titration in ethylene-glycol-isopropanol solvent has recently been adapted to the determination of carboxylic acid salts (3, 4). Salts of high molecular weight fatty acids, such as the soaps, are commonly analyzed by acidification followed by ethyl ether extraction of the water-insoluble fatty acid (5).

The use of cation exchange resins for the determination of salts of organic acids has been reveiwed by Samuelson (6). Van Etten and Wiele employed Dowex 50 resin to convert organic salts to the free acids (7). These studies were concerned mainly with the determination of short chain, polybasic, and aromatic acids.

A rapid method for the determination of soap in the presence of neutral fat was desired. The use of cation exchange resins with organic solvents proved successful. The analysis of pure soap solutions prepared from authentic fatty acids was studied. Conversion of soap to fatty acid averaged 99.80% recovery. A single determination could be run in 20–30 min. The soap in a series of commercial products was also determined by the method. The total fatty acid values were compared with values obtained by extraction and titration.

Materials Required

Dowex 50 ion exchange resin

Chamber burette, 100-ml. capacity

The neck above the chamber is removed, leaving a reservoir of approximately 45 ml. above the graduated burette.

Standardized 0.1N alcoholic sodium hydroxide
Standardized 0.1N alcoholic potassium hydroxide
Phenolphthalein indicator, 1% in 95% Alcohol
Ethyl alcohol, formula 3A containing 5% methanol and 5% water
Benzene, C. P.

Column Preparation

The resin was prepared for use by allowing 50 g. to stand overnight in 6N hydrochloric acid. It was washed 6 times by decantation with 200-ml. volumes of distilled water. A volume of 200 ml. of 50% alcohol was added to the resin and allowed to remain in contact for 1 hr. The resin was then washed six times with 50% alcohol and twice with 95% alcohol by decantation.

A glass wool plug 2 cm. in length was placed next to the stopcock in the burette. The burette was filled with alcohol, and the resin was added slowly with tapping. A bed of approximately 45 ml. of resin was added. Alcohol was then passed through the column until 150 ml. of effluent consumed no more than 0.3 ml. of 0.1N caustic.

A column so prepared has a total capacity of 90 milliequivalents. In actual practice the resin was replaced after 15-20 milliequivalents had been passed through. No attempt to test the effective capacity of the column was made.

Analysis of Synthesized Soap

A 0.2- to 0.5-g. sample of fatty acid was placed in a 150-ml. beaker and dissolved in 20–30 ml. of alcohol. Three drops of phenolphthalein indicator were added, and the fatty acid was titrated to the first permanent pink with standard alcoholic base. The volume of base was recorded, and the milliequivalents of soap formed was calculated. This alcoholic soap solution was then passed through the column at a rate of 6–8 ml. per minute. It was followed by 100 ml. of alcohol.

The effluent, totaling *ca.* 150 ml., was collected in a 250-ml. Erlenmeyer flask. Three drops of phenolphthalein indicator solution were added, and the fatty acid was titrated with the same strength base used to form the soap. The volume was recorded, and the milliequivalents of fatty acid were calculated. A blank amounting to the total volume of alcohol in the effluent was passed through the column and titrated. This value was subtracted from the final titration.

Results

The conversion and subsequent analysis of 13 soaps are presented in Table I. Average recovery was 99.80%. The lauric, myristic, and palmitic acids were

TABLE I
Conversion and Analysis of Typical Synthesized Soaps

Soap	Milli-equivalents Added	Milli-equivalents Recovered	% Recovered
Potassium heptanoate	3.234	3.216	99.44
Potassium pelargonate	3.938	3.927	99.72
Potassium caprate	1.710	1.702	99.53
Sodium undecylenate	3.843	3.843	100.00
Potassium laurate	2.055	2.060	100.24
Sodium laurate	1.959	1.959	100.00
Potassium myristate	2.278	2.277	99.96
Potassium palmitate	1.149	1.143	99.48
Sodium palmitate	1.097	1.097	100.00
Potassium stearate	1.785	1.789	100.22
Sodium oleate	1.157	1.143	98.79
Potassium oleate	2.550	2.550	100.00
Potassium linoleate	2.974	2.974	100.00

Average Recovery = 99.80%.

TABLE II
Analytical Results on Commercial Products

Sample	Total Fatty Acid by Ion Exchange	Total Fatty Acid by Extraction and Titration	Solvent
Brushless Shave Cream No. 1 [a]	19.35	19.29	Ethanol-Benzene 1:1
Brushless Shave Cream No. 2 [b]	22.72	22.35	Ethanol-Benzene 1:1
Brushless Shave Cream No. 3 [c]	26.05	26.56	Ethanol-Benzene 1:1
Soap Facial Cleanser [d]	33.70	33.67	Ethanol
Shampoo No. 1	29.65	29.06	Ethanol
Shampoo No. 2 [e]	12.91	12.70	Ethanol
Commercial Soap Flakes [f]	87.85	87.92	Ethanol-Benzene 1:1

[a] Includes 15.50% free fatty acid.
[b] Includes 19.87% free fatty acid.
[c] Includes 21.90% free fatty acid.
[d] Includes 4.42% free fatty acid.
[e] Phosphate removed as alcohol insoluble before analysis.
[f] Corrected for 0.549% NaCl.

obtained from saponification of methyl esters distilled in this laboratory. The remaining fatty acids were obtained from commercial sources. Neutralization equivalents indicated the composition of all samples to be as represented.

Analysis of Commercial Soap Products

Products based on soap as the active ingredient or as an emulsifier were analyzed for total fatty acid by ion exchange conversion. The procedure was similar to that used for pure soaps; a single determination consumed less than 30 min. Table II presents the results obtained on shaving creams, shampoos, soap flakes, and a facial cleanser. It was found necessary to remove salt impurities, such as sulfates and phosphates, as alcohol-insoluble matter before passage through the resin. When chloride was present, the appropriate correction was made. Such additional steps increase the time required per determination.

Borax, which occurs in many shaving creams, is converted to boric acid by the cation exchange resin. This does not constitute an interference *per se,* but in the presence of glycerol, which is also a component of shaving products, the acidic complex is formed and high results are obtained.

A benzene-ethanol 1:1 mixture was found to be a suitable solvent for super-fatted products where complete solubility was not possible with ethanol alone.

Acknowledgment

The author is indebted to E. W. Blank for his interest and encouragement in this work.

REFERENCES

1. Niederl, J. B., and Niederl, V., "Organic Quantitative Microanalysis," 2nd ed., pp. 62–65, John Wiley and Sons Inc., New York (1942).
2. Siggia and Maisch, Ind. Eng. Chem. (Anal. Ed.), *20*, 235–236 (1948).
3. Palit, S., Ind. Eng. Chem. (Anal. Ed.), *18*, 246–251 (1946).
4. Siggia, S., "Quantitative Organic Analysis via Functional Groups," 2nd ed., pp. 42–44, John Wiley and Sons Inc., New York (1954).
5. Official and Tentative Methods of the American Oil Chemists' Society, Method Da 8–48.
6. Samuelson, O., "Ion Exchange in Analytical Chemistry," pp. 129–130, John Wiley and Sons Inc., New York (1953).
7. Van Etten and Wiele, Anal. Chem., *25*, 1109–1111 (1953).

[Received October 17, 1955]

ABSTRACTS . . . .

R. A. Reiners, Editor

• Oils and Fats

S. S. Chang, Abstractor
Sini'tiro Kawamura, Abstractor
Dorothy M. Rathmann, Abstractor

The alkali-catalysed isomerization of unsaturated compounds. J. B. Davenport, A. J. Birch and A. J. Ryan (Dept. of Org. Chem., Univ. of Sydney). *Chem. and Ind.* **1956**, 136–7. The ultraviolet absorption curves of *cis*-unsaturated acids after isomerization by refluxing with a molar solution of potassium tert.-butoxide in tert.-butanol are considered as bases of an empirical estimation method for these acids. This reagent has advantages over the standard glycol reagent. The blanks are completely transparent and after maximum conjugation is achieved there is no destruction of product. The technique is also very simple. Application of this method to the kinetic study of isomerization of *cis*-unsaturated fatty acids shows the expected first order constants, and demonstrates also that the 1,4,7-trienes have a lower Arrhenius activation energy (approx. 13 k. cal. per mole) for conjugated diene production than do the 1,4-dienes (approx. 20 k. cal. per mole).

The structure and reactions of gossypol. III. Aliphatic anil derivatives of gossypol. D. A. Shirley and W. C. Sheehan (Dept. of Chem., Univ. of Tenn., Knoxville, Tenn.). *J. Org. Chem.* **21**, 251–2 (1956). Stable anils of gossypol with primary aliphatic amines of 2, 5, 10, 14, 16, and 18 carbons were prepared. Their melting points were 251–255° (d), 218–221° (d), 164.5–165.5°, 126.5–127°, 116–116.5°, and 112.5–113°, respectively.

Constitution of isanic and isanolic acids. A. Seher (Univ. Münster, Ger.). *Ann.* **589**, 222–38 (1954). In studying the structures of isanic acid and isanolic acid isolated from Isano-(or Boleko) seed oil, a series of conjugated diene dicarboxylic acids were prepared and their properties studied. The collected data show unequivocally that isanic acid has the structure $CH_2=CH(CH_2)_4-C\equiv CC\equiv C(CH_2)_7COOH$. Based on the present data and those reported previously, the structure of isanolic acid is $CH_3(CH_2)_2CH=CHC\equiv CC\equiv CCH_2CH(OH)\text{-}(CH_2)_6COOH$. (*C. A.* **50**, 1601)

Electrolysis of organic acids and the decomposition of diacyl peroxides. III. The electrolysis of free fatty acid and the decomposition of diacyl peroxides in pyridine. S. Goldschmidt and M. Minsinger (Tech. Hoch-schule, Munich, Ger.). *Chem. Ber.* **87**, 956–63 (1954). Acetic, propionic, and butyric acid were electrolyzed in pyridine or *α*-methylpyridine. The electrolysis of fatty acids in pyridine and the decomposition of acyl peroxides in pyridine produced similar results. The products of electrolyses were fractionated and characterized. (*C. A.* **50**, 334)

Liver oil of Centrophorus grandulosus. I. Isolation of squalene from the unsaponifiable matter. F. Ramos Ayerbe and M. A. Albi Romero. *Grasas y aceites* (Seville, Spain), **6**, 141–3 (1955). The liver of *C. granulosus* constitutes about 23% of the weight of its body and contains 60–75% oil. The liver oil has the following characteristics: d^{25}, 0.8682; n_D^{25}, 1.4900; acid number, 1.3; saponification number, 29.0; iodine number, 260; hydroxyl number, 4. The unsaponifiable matter was a clear yellow liquid. By chromatography on an alumina column, a colorless liquid similar to squalene was separated from the unsaponifiable matter. A similar fraction was also obtained by distillation in vacuo of the unsaponifiable matter. (*C. A.* **50**, 2192)

Methods of differentiation between refined and unrefined fats and oils. S. H. Bertram. *Rev. fermentations et ind.* **10**, 165–6 (1955). This method for differentiating between refined and unrefined fats and oils is based on measurements of the electric conductance of the dry material at 100°. The electric conductances of several crude and refined fats and oil were determined by the method described. (*C. A.* **50**, 2189)

23rd annual short course for oil mill operators. I. What's new in oil milling. M. C. Verdery, *et al. Oil Mill Gaz.* **60**(4), 11–14, 16, 18–22 (1955). New devices applicable in milling are illustrated and described. **Cottonseed cleaning experiments.** S. P. Clark. *Ibid.* 22. **Separation of cottonseed by projection**